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1 RUBBER COMPOSITION AND RUBBER HOSE THEREFROM

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(54) RUBBER COMPOSITION AND RUBBER HOSE THEREFROM

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a rubber composition which contains hydrogenated NBR, zinc dimethacrylate and/or zinc diacrylate, an epoxy compound and an organic peroxide vulcanizer and shows excellent vulcanizing adhesion to brass or zinc as well as holds resistance to oil and heat.

SOLUTION: This rubber composition comprises (A) hydrogenated NBR (preferably an acrylonitrile/butadiene random copolymer having 25-45wt.% acrylonitrile content is hydrogenated to a $\geq 95\%$ hydrogenation rate and has a Mooney viscosity of 40-100), (B) zinc dimethacrylate and/or zinc diacrylate, (C) an epoxy compound (preferably a glycidyl ether type epoxy resin with an epoxy equivalent of 120-300) and (C) an organic peroxide vulcanizer (preferably a dialkyl peroxide with a half life of 10 hours at $\geq 80^\circ\text{C}$). In a preferred embodiment, the component in an amount of 100 pts.wt. A is formulated with 50-150 pts.wt. of the component B, 5-30 pts.wt. of the component C and 1-10 pts.wt. of the component C.

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

[Claim(s)]

[Claim 1] The rubber constituent containing Hydrogenation NBR, zinc dimethacrylate and/or diacrylic acid zinc, an epoxy compound, and an organic peroxide vulcanizing agent.

[Claim 2] The content rate of each component of said rubber constituent is zinc dimethacrylate and/or diacrylic acid zinc to the hydrogenation NBR 100 weight section. The 30 - 200 weight section, epoxy compound 5 - 30 weight section and organic peroxide vulcanizing agent Rubber constituent according to claim 1 which is 0.1 - 10 weight section.

[Claim 3] The rubber hose this whose inner tube is vulcanizate of the rubber constituent of claims 1 or 2 at least in the rubber hose which it comes to constitute from the reinforcement layer and outer tube which consist of an inner tube and brass plating ****.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention uses hydrogenation NBR as a rubber component, and relates to the rubber constituent excellent in the vulcanization adhesive property with brass. Furthermore, an inner tube is related with the rubber hose which is vulcanizate of the rubber constituent at least.

[0002]

[Description of the Prior Art] Also while the vulcanizate of Hydrogenation NBR is excellent in oilproof and thermal resistance in itself, the vulcanizate of the rubber constituent (for example, sold as a trade name ZSC from Nippon Zeon Co., Ltd.) which blended zinc dimethacrylate and/or diacrylic acid zinc, and organic peroxide is excellent in reinforcement, thermal resistance, and oilproof as a vulcanization system.

[0003] However, the rubber constituent which uses this hydrogenation NBR as a rubber component does not have an enough vulcanization adhesive property with brass. Therefore, the application to products, such as the tire and belt using the steel wire which galvanized brass or zinc as a reinforcement layer, a roll, a molded product, and a hose, was restricted naturally.

[0004]

[Problem(s) to be Solved by the Invention] In this way, the purpose of this invention is offering the vulcanizate of offering the rubber constituent excellent in the vulcanization adhesive property with brass or zinc, and this constituent, employing efficiently oilproof and thermal resistance which hydrogenation NBR vulcanizate originally has.

[0005] Moreover, another purpose of this invention is having the reinforcement layer whose front face's is brass or zinc, and offering the rubber hose using the vulcanizate of the above-mentioned rubber constituent as an inner tube at least.

[0006]

[Means for Solving the Problem] The rubber constituent which blended Hydrogenation NBR, zinc dimethacrylate, diacrylic acid zinc or those mixture, the epoxy compound, and the organic

peroxide vulcanizing agent found out excelling in reinforcement and excelling in a vulcanization adhesive property with brass moreover, and the artificers of this invention completed this invention. That is, according to the 1st mode of this invention, the rubber constituent containing Hydrogenation NBR, zinc dimethacrylate and/or diacrylic acid zinc, an epoxy compound, and an organic peroxide vulcanizing agent is offered. Furthermore, according to another mode of this invention, in the rubber hose which it comes to constitute from the reinforcement layer and outer tube which consist of an inner tube, brass, or galvanization ****, the rubber hose the inner tube of whose is vulcanizate of the rubber constituent of this invention at least is offered.

[0007] Hereafter, although the configuration of this invention is explained in full detail, the advantage based on a mode and it with desirable this invention will become clear. The 1st mode of this invention is the rubber constituent which blended Hydrogenation NBR, zinc dimethacrylate, diacrylic acid zinc or those mixture, the epoxy compound, and the organic peroxide vulcanizing agent.

[0008] As for the zinc dimethacrylate, the diacrylic acid zinc, or those mixture of this invention, it is desirable the 30 - 200 weight section and to carry out 50-150 weight section combination from the point of reinforcement and rubber elasticity especially with the total quantity to the hydrogenation NBR100 weight section. Specifically, commercial items, such as R-20S by the Asada chemical-industry company and CPR, can be used.

[0009] As an epoxy compound of this invention, it has at least two or more epoxy groups in 1 molecule, and the epoxy resin of the glycidyl ether mold of 120-300 has [100 or more] especially desirable weight per epoxy equivalent. The reaction of Hydrogenation NBR, zinc dimethacrylate or diacrylic acid zinc, and an epoxy resin and organic peroxide advances in concertante performance that it is this range, and a desirable result is obtained at the point which adhesive strength with the reinforcement plating steel wire of an epoxy resin can demonstrate to the maximum extent. As an example of a glycidyl ether mold epoxy resin, the glycidyl ether of a dihydric phenol especially the poly glycidyl ether of bisphenol A, the poly glycidyl ether of Bisphenol F, etc. are desirable. Moreover, the commercial item of the SUMIEPOKISHI ELA115 grade by Sumitomo Chemical Co., Ltd. can be used.

[0010] using an epoxy compound for this invention -- the crosslinking reaction of the rubber of Hydrogenation NBR, zinc dimethacrylate or diacrylic acid zinc, and organic peroxide -- in addition, it is further placed between reactions by the epoxy compound, and while raising the physical properties of a constituent, in order that the epoxy group of this epoxy compound may combine with the brass of reinforcement steel wire, or a zincky surface layer strongly with the polarity of an epoxy group, it becomes possible to discover adhesive strength, holding high physical properties to oilproof, thermal resistance, etc.

[0011] With the hydrogenation NBR of this invention, hydrogen adds to the carbon with which an acrylonitrile unit content has a double bond preferably 15 to 50% of the weight among the random copolymers of 25 - 45% of the weight of acrylonitrile, and a butadiene. The rate of hydrogenation is usually 95% or more preferably 80% or more. Moreover, as for Mooney viscosity (ML 1+4, 100 degrees C), it is desirable that it is 40-100. Specifically, it is Zetpol by Nippon Zeon Co., Ltd. The commercial item of the 2000th grade can be used.

[0012] In a rubber constituent, if the organic peroxide vulcanizing agent used for this invention is organic peroxide with which crosslinking reaction does not advance to the degree of pole at the temperature at the time of processing, any are sufficient as it, and its dialkyl peroxide whose decomposition temperature a half-life is 80 degrees C or more preferably in 10 hours is good. For example, a JIKUMIRUPAO side, 1, 3-screw-(tert-butyl peroxide-isopropyl) benzene, 4, 4-G

tertiary-butyl par OKISHIBA relic acid n-butyl, etc. are mentioned. Specifically, the commercial item of parka DOKKUSU 14 / 40 grades by powder Akzo can be used. As for these vulcanizing agents, it is especially desirable to the hydrogenation NBR100 weight section 0.1 - 20 weight section and that it is 1 - 10 weight section. If it is this range, it is desirable at the point that the above-mentioned reaction is maintainable proper, it excels in physical properties and the good relation of adhesion can be maintained.

[0013] The compounding agent of others, such as a plasticizer, a reinforcing agent, a degradation inhibitor, and a coloring agent, other than the above-mentioned compounding agent may be added in the range which does not check the property of the rubber constituent of this invention. Moreover, although either is usable if it is the accelerator of the organic peroxide generally used as a vulcanization assistant and an accelerator, acrylate, little sulfas donors, etc., such as cyanuric acid, such as triallyl isocyanurate and a triaryl SHIANU rate, and trimethylolpropanetrimethacrylate, can be used.

[0014] 100-200 degrees C is [that what is necessary is just to carry out melting kneading of the manufacture of the rubber constituent of this invention with the usual Banbury mixer etc.] suitable for kneading temperature.

[0015] Succeedingly, a roll processing process or after adding a vulcanizing agent with a Banbury mixer etc. similarly, adjusting a uniform unvulcanized constituent and fabricating in a desired configuration, at the temperature of 130-200 degrees C, it vulcanizes by vulcanizing by heating for 10 - 90 minutes, or heating by said temperature and said time amount to shaping and coincidence, and the vulcanizate of the rubber constituent of this invention can be obtained.

[0016] In this way, the vulcanizate of the rubber constituent of obtained this invention can be excellent in disruptive strength, thermal resistance, and oilproof, and, moreover, vulcanization adhesion can be carried out with metals, such as brass and zinc, and it can form the complex of a metal/vulcanized rubber.

[0017] The rubber constituent of this invention and its vulcanizate, and the metal to paste up are used for the usual rubber goods as reinforcing materials, and may take gestalten, such as a wire rod, a tubing material, and a plate. Brass, the steel which carried out brass plating, zinc, the galvanized steel wire, copper, bronze, aluminum, iron, etc. are mentioned, and brass, the steel which carried out brass plating, zinc, and the galvanized steel wire are suitable for the class of metal to be used also in it.

[0018] The 2nd mode of this invention is related with the rubber goods which used the vulcanizate of the rubber constituent of this invention. When a pressure joins these rubber goods or it is an elevated temperature, the disruptive strength of the material itself, thermal resistance, and the product that was excellent in respect of oilproof are useful, but when an adhesive property with the member for reinforcing this is high, endurance improves to the flow stress applied and the usefulness as a product is still higher.

[0019] A belt, a roll, a molded product, a hose, etc. are mentioned as an example of the product using the rubber constituent of this invention, and its vulcanizate. Here, this invention is not limited by this although a hose is shown and explained to drawing 1 as one of them.

[0020] It comes to constitute the rubber hose 1 shown in drawing 1 from an inner tube 2, a reinforcement layer 3, and an outer tube 4, and said inner tube 2 is formed with the vulcanizate of the rubber constituent of this invention. The diameter of tubing of the rubber hose of this invention is about 5-50mm that what is necessary is just the range of the usual rubber hose.

[0021] The inner tube 2 contacted fluids, such as a liquid which moves the inside of a rubber hose 1, and directly, and has stuck the reinforcement layer 3, and, as for thickness, it is desirable

that it is about 0.3-5mm.

[0022] The reinforcement layer 3 was stuck with the inner tube 2, is stuck to the outer tube 4, and is an independent layer of metal wires, such as brass, a rope by which brass plating was carried out, or galvanized steel. Moreover, you may consist of two or more layers which allotted by turns the reinforcement layer and the layer of the vulcanizate which includes the vulcanizate of the rubber constituent of this invention. Moreover, if it is the range which does not bar the property of the rubber hose of this invention, there will be no limitation especially in a metaled gestalt.

[0023] The outer tube 4 has stuck with the reinforcement layer 3, prevents breakage of the inner tube 2 by the impact, heat, etc., and the reinforcement layer 3, and fixes the reinforcement layer 3. Moreover, as long as it is the range which does not bar the property of the rubber hose of this invention, said outer tube 4 may be the rubber constituent of this invention, and may be vulcanizate of what kind of rubber constituent. For example, the vulcanizate of rubber, such as chloroprene rubber (CR), isobutylene isoprene rubber (IIR, Cl-IIR, Br-IIR), SBR, ethylene propylene copolymerization rubber (EPM, EPDM), chlorinated polyethylene (CM), chlorosulfonated polyethylene (CSM), HIDORINGOMU (CHC, CHR), and an isobutylene-bromination PARAME chill styrene copolymerization object, can be mentioned.

[0024] After the rubber hose of such a configuration can adopt a well-known approach in itself, for example, twisting the constituent of this invention around a mandrel, preparing a reinforcement layer on it succeedingly and then twisting the rubber constituent for outer tubes, it is manufactured by [which attached sheaths, such as lead, if needed] carrying out after cure.

[0025]

[Example] This invention is not restricted by this, although an example and the example of a comparison are shown and this invention is explained concretely hereafter.

[0026] (Examples 1-8 and examples 1-5 of a comparison) It kneaded for 5 minutes with the Banbury mixer at a rate given [the component except organic peroxide] in Table 1, among the components of a publication to Table 1, organic peroxide was fully kneaded with the roll for rubber the appropriate back, and ***** was performed in the thickness of 2.5mm. The obtained sheet was used, pressurization heating of the brass plate of 15cmx15cmx2mmt and the sheet of the same magnitude (15cmx15cm) as the brass plate was carried out for 160 degree-Cx 30 minutes using superposition and mold, and the complex of brass/vulcanized rubber was manufactured. On the other hand, the mold of 15cmx15cmx2mmt was used, the sheet which vulcanized this sheet for 160 degree-Cx 30 minutes was created, and the physical properties were measured. The result of the adhesion to brass and physical properties was shown in Table 1. Moreover, the rubber of Table 1 is extruded on a mandrel with the extruder for rubber of a crosshead. Covering (outer layer) of CR is further covered with the crosshead extruder for rubber after a braid with a brass plating wire after an appropriate time. After wrapping with cloth, a steam vulcanizer is used for the vulcanization for 160 degree-Cx 60 minutes. The hose was made to vulcanize, after removing a wrapping cloth, the mandrel was extracted, the hose which has the bore of 10mm shown in drawing 1 , 1.5mm of tube thickness, an inner tube with an outer diameter of 13mm, a brass plating wire reinforcement layer, and an outer tube with an outer diameter of 19mm was created, and the adhesion force and impulse endurance were evaluated.

[0027]

[Table 1]

表 1 (その1)

| | | | 比較例 1 | 比較例 2 | 比較例 3 | 比較例 4 | 比較例 5 |
|------------------|---------------------------------------|----|----------|----------|----------|----------|----------|
| 配合組成 (重量部) | 水素化NBR | *1 | 100 | 100 | 100 | 100 | 100 |
| | ジタメクリル酸亜鉛 | *2 | 35 | 50 | | 200 | 250 |
| | ジアクリル酸亜鉛 | *3 | | | 50 | | |
| | ビスフェノールAの ジグリシジルエーテル | *4 | — | — | — | — | — |
| | 有機過酸化物加硫剤 | *5 | 8 | 8 | 8 | 8 | 8 |
| 常態物性 | 引張り強さ T_b (kg/cm ²) | | 370 | 420 | 400 | 530 | 420 |
| | 破断伸び E_b (%) | | 260 | 350 | 330 | 430 | 430 |
| | モジュラス M_{100} (kg/cm ²) | | 55 | 40 | 35 | 30 | 17 |
| | JIS硬度 H_a | | 75 | 70 | 70 | 65 | 62 |
| 真鍮接着性 | | | | | | | |
| 剥離力 (kgf/25mm) | | | 0 | 0 | 0 | 0 | 0 |
| ゴム付き (%) | | | 0 | 0 | 0 | 0 | 0 |
| ホース性能評価 (高温衝撃試験) | | | | | | | |
| インパルス耐久回数 (万回) | | | 未 | <0.1 | <0.1 | 未 | 未 |

(表1中の配合成分の説明)

*1 zetpol 2000 日本ゼオン(株)製
*2 R-20S 浅田化学工業社製
*3 CPR 浅田化学工業社製

*4 スミエポキシ ELA-115 住友化学工業(株)製
*5 パーカドックス14/40 火薬アクト社製

[0028]

[Table 2]

表 1 (その2)

| | | 実施例 1 | 実施例 2 | 実施例 3 | 実施例 4 | 実施例 5 | 実施例 6 | 実施例 7 | 実施例 8 |
|------------------|---------------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|
| 配合組成 (重量部) | 水素化NBR *1 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | ジタメクリル酸亜鉛 *2 | 35 | 50 | | 200 | 50 | 200 | 250 | 200 |
| | ジアクリル酸亜鉛 *3 | | | 50 | | | | | |
| | ビスフェノールAの シグリシジルエーテル *4 | 5 | 5 | 5 | 5 | 30 | 30 | 5 | 40 |
| | 有機過酸化化合物加硫剤 *5 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| 常態物性 | 引張り強さ T_b (kg/cm ²) | 350 | 400 | 380 | 510 | 360 | 410 | 240 | 240 |
| | 破断伸び E_b (%) | 250 | 340 | 320 | 420 | 210 | 290 | 120 | 120 |
| | モジュラス M_{100} (kg/cm ²) | 70 | 55 | 50 | 45 | 92 | 81 | 21 | 135 |
| | JIS硬度 H_s | 80 | 75 | 75 | 70 | 89 | 82 | 64 | 95 |
| 真鍮接着性 | | | | | | | | | |
| 剥離力 (kgf/25mm) | | 15 | 18 | 18 | 21 | 21 | 20 | 12 | 20 |
| ゴム付き (%) | | 90 | 100 | 100 | 100 | 95 | 95 | 50 | 70 |
| ホース性能評価 (高温衝撃試験) | | | | | | | | | |
| インパルス耐久回数 (万回) | | >100 | >100 | >100 | >100 | >100 | >100 | 11 | 15 |

(表1中の配合成分の説明)

- | | | | |
|----------------|-----------|-------------------|------------|
| *1 zetpol 2000 | 日本ゼオン(株)製 | *4 スミエポキシ ELA-115 | 住友化学工業(株)製 |
| *2 R-20S | 浅田化学工業社製 | *5 パーカドックス14/40 | 火薬アクゾ社製 |
| *3 CPR | 浅田化学工業社製 | | |

[0029] In addition, the physical properties of an example and the example of a comparison were measured by the approach shown below. A result is shown in the above-mentioned table 1.

- (1) Exfoliation force JIS K The exfoliation force was measured by 6301-8.
- (2) JIS with rubber K It measured with rubber by covering % of the rubber on the brass plate of the sample which exfoliated by 6301-8.
- (3) Tensile strength JIS K Tensile strength was measured by 6301-3.
- (4) Elongation-after-fracture JIS K Elongation after fracture was measured by 6301-3.
- (5) Modulus JIS K By 6301-3, the modulus at the time of 100% expanding was measured.
- (6) JIS hardness JIS K JIS hardness was measured by 6301-5.
- (7) A hose performance-evaluation test condition is SAE 11B8. Based on TYPE1, temperature was carried out at 140 degrees C. It is desirable that the count of impulse durability is 1 million times or more. Front Naka and the "sheep" show having not examined. The above example shows the vulcanizate which is excellent in reinforcement and an elastic modulus being obtained from the constituent of this invention, and excelling in the vulcanization adhesive strength to

brass moreover.

[0030]

[Effect of the Invention] The rubber constituent of this invention is excellent in a vulcanization adhesive property with a metal, especially brass. The complex of a metal (especially brass)/vulcanized rubber excellent in the adhesive property is manufactured by this. Therefore, the outstanding rubber goods which have a reinforcement layer are manufactured by the interior, such as a tire, a belt, a roll, a molded product, and a hose, from the constituent of this invention. When the vulcanizate of this invention is used as an inner tube of the rubber hose which requires oilproof especially, the rubber hose which the adhesive property with the metal member of a reinforcement layer is improved, and was excellent is offered.

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the layer structure of a rubber hose notionally.

[Description of Notations]

- 1 Rubber Hose
- 2 Inner Tube
- 3 Reinforcement Layer
- 4 Outer Tube

